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MOBILITY COEFFICIENTS IN THE SYSTEMS OF MAGNETIC DIPOLAR PARTICLES

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In this paper, we present our first results on the mobility coefficients in the systems of magnetic dipolar particles. In our study, we investigate the influence of chain formation and polydispersity of particles on self-diffusion. The work is purely theoretical and combines direct calculations with the density functional approach to calculate equilibrium densities of chains. We study mainly bulk systems. It is shown that the formation of chains leads to the average decrease of mobility in monodisperse systems, but in the case of bidisperse particle size distribution, the particle mobility becomes a function of the fractional composition. The mobility coefficients obtained here are important for calculating the diffusion coefficients in case of gradient-induced diffusion (be that of the field or density gradient) in magnetic fluids with chain aggregates.

Introduction. Magnetic fluids (ferrofluids) are systems consisting of single-domain magnetic particles suspended in a carrier liquid [1]–[3]. Real ferrofluids have a complex and sufficiently versatile microstructure related to the non-central interparticle interaction, i.e. the magnetic dipole-dipole interaction [4]:

$$U_{\mathrm{dd}}(i,j) = \frac{\mu_0}{4\pi}\left(\frac{\langle \boldsymbol{\mu}_i, \boldsymbol{\mu}_j\rangle}{|\mathbf{r}_{ij}|^3} - \frac{3}{|\mathbf{r}_{ij}|^5}\langle \boldsymbol{\mu}_i, \mathbf{r}_{ij}\rangle\langle \boldsymbol{\mu}_j, \mathbf{r}_{ij}\rangle\right),$$

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are the magnetic moments of i^{th} and j^{th} particles, respectively; $\mathbf{r}_{ij}$, $|\mathbf{r}_{ij}| = r_{ij}$, is the vector connecting the centers of i^{th} and j^{th} particles, $\mu_0 = 4\pi \times 10^{-7}$ H/m is the magnetic permeability of vacuum.

The magnetic dipole-dipole interaction parameter is the ratio of magnetic-to-thermal energy (kT):

$$\lambda_{ij} = \frac{\mu_0 \mu_i \mu_j}{4\pi k T r_{ij}^3}.$$

To describe the interparticle repulsion of "soft sphere" type, the Weeks–Chandler–Andersen potential [5] is used:

$$U_{WCA}(i,j) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right] + \varepsilon, & r \le r_c, \\ 0, & r > r_c, \end{cases}$$

where ε is the potential well depth, σ is a distance when the interaction energy becomes equal to zero.

Ferrofluids have many applications, in particular, in medicine. Diffusion properties are important in medical applications. For the effective use of magnetic dipolar systems, it is necessary to know self-diffusion coefficients [6]–[10]. There were several works investigating the diffusion in magnetic fluids [11]–[15], however, the detailed theoretical description is still missing.

1. Chain formation in magnetic fluids: density functional theory. In our research we consider two systems. The first system is a monodisperse model with chain aggregates. It consists of chains of different length and the magnetic particles of the system are identical. The second system is a bidisperse ferrofluid with chains. It is composed of particles of two types. We will call them small and large ones. The microstructure of the bidisperse system is more complex than that of the monodisperse model: it contains three classes of chain aggregates and also single small and large particles. The first chain class corresponds to chain aggregates consisting of large particles only. The chain aggregates of the second class are chains consisting of large particles with one small particle at the end of the chain, and the third chain class is composed of chain aggregates consisting of large particles with two small particles at the ends of the chain. All particles in the systems have a thin non-magnetic layer of surfactant (of approximately 2 nm thick).

The basis of our theory is the free energy density functional. In the monodisperse system, the free energy density functional has the following form [16]:

$$F = kT \sum_{n=1}^{\infty} g(n) \left(\ln \frac{g(n)v(n)}{e} - \ln Q(n) \right),$$

where $g(n)$ is the concentration of chains consisting of n particles, $v(n) = v$ is the normalizing volume equal to the particle volume, $Q(n)$ is the chain statistical sum. Also, there is a mass-balance constraint on the total number of particles in the system:

$$\frac{\rho}{v} = \sum_{n=1}^{\infty} n g(n),$$

where ρ is the particle concentration.

In the bidisperse system, the free energy density functional and the mass-balance constraints on the total number of small and large particles in the system can be written as [17]:

$$F = kT \sum_{n+m\geq 1}^{\infty} \sum_{i=1}^{I(n,m)} K(i,n,m) g(i,n,m) \left[\ln \frac{g(i,n,m)v(i,n,m)}{e} - \ln Q(i,n,m) \right];$$

$$\frac{\rho_s}{v_s} = \sum_{n+m\geq 1}^{\infty} \sum_{i=1}^{I(n,m)} K(i,n,m) g(i,n,m) m,$$

$$\frac{\rho_l}{v_l} = \sum_{n+m\geq 1}^{\infty} \sum_{i=1}^{I(n,m)} K(i,n,m) g(i,n,m) n,$$

where $K(i,n,m)$ is a combinatorial multiplier responsible for the number of entropy different chains consisting of m small and n large particles in the i^{th} chain class, $g(i,n,m)$ is the chain concentration, $v(i,n,m)$ is the normalizing volume, $Q(i,n,m)$ is the chain statistical sum, ρ_s and ρ_l are the volume concentrations of small and large particles, respectively, v_s and v_l are the volumes of small and large particles, respectively.

We perform the functional minimization under the mass-balance constraints using the Lagrange multiplier method. After that we obtain chain aggregate concentrations. Now we can discuss the microstructure using these concentrations. In particular, we can obtain an average chain length. It is known that in the

monodisperse model the average number of large particles in a chain increases with the increasing particle concentration, and in the bidisperse ferrofluid the average chain length decreases with the increasing small particle concentration. So the microstructures of the systems are different, hence, average mobilities also differ.

2. Mobility coefficients. For computing average mobilities of the systems, we have approximated the chain aggregates by ellipsoids. We can obtain average mobilities $\langle M \rangle$ of ellipsoids using the formulas, which were analytically derived by Perrin [18]:

$$\langle M \rangle = \left[6\pi\eta b \frac{G_a(p) + G_b(p)}{2} \right]^{-1},$$

$$G_a(p) = \frac{8}{3} \left[\frac{2p}{1-p^2} + \frac{2p^2-1}{(p^2-1)^{\frac{3}{2}}} \ln \frac{p+\sqrt{p^2-1}}{p-\sqrt{p^2-1}} \right]^{-1},$$

$$G_b(p) = \frac{8}{3} \left[\frac{p}{p^2-1} + \frac{2p^2-3}{(p^2-1)^{\frac{3}{2}}} \ln \left(p+\sqrt{p^2-1} \right) \right]^{-1},$$

where a is the major semi-axis, b is the minor semi-axis, $p = a/b$ is the aspect ratio of the semi-axes, G_a and G_b are the geometric factors characterizing the amount of deviations of the ellipsoid from a sphere, η is the viscosity. In our study, we consider the ratio of the average mobilities of ellipsoids to the average mobility of the chain aggregate with one large particle ($\langle M_0 \rangle$). In other words, we investigate effective average mobilities.

3. Results and discussion. As mentioned above, we study the monodisperse and bidisperse systems. Using the formulas given in the previous section, we can show how the effective average mobilities of the systems change depending on different parameters. Even though the average mobility is not directly related to the diffusion coefficient, when studying the density- or the field-gradient driven diffusion, one needs to know the mobility as a coefficient relating two various expressions for the flux [19].

Now, we can derive formulas for computing the effective average mobilities. The microstructure of the monodisperse model is composed of chains consisting of n particles. These chains can be approximated by ellipsoids with $a = nd$ and $b = d$ (d is the particle diameter). Hence, we can assume that the aspect ratio is equal to $p = n$. Thus, the effective average mobility for the monodisperse system has the following form:

$$\frac{\langle M \rangle}{\langle M_0 \rangle} = \frac{(1 - P(\lambda, \rho))}{P(\lambda, \rho)} \left\{ \sum_{k=2}^{\infty} \left[P^k(\lambda, \rho) \left(\frac{G_a(k) + G_b(k)}{2} \right)^{-1} \right] + P(\lambda, \rho) \right\},$$

where $P(\lambda, \rho)$ is the probability of particle pair formation found from the energy minimization (see, Section 2).

For the bidisperse system, three chain classes are distinguished, so the aspect ratio and the major semi-axis will depend on the topological index i. Let the small particles have the diameter d_{S} and the diameter of large particles is d_{L}. Then for the first class of chains we have $a(1) = nd_{\mathrm{L}}$ and $b = d_{\mathrm{L}}$, so $p(1) = n$. For the second chain class, there are $a(2) = nd_{\mathrm{L}} + d_{\mathrm{S}}$, $b = d_{\mathrm{L}}$ and $p(2) = (nd_{\mathrm{L}} + d_{\mathrm{S}})/d_{\mathrm{L}}$; and for the third chain aggregate class, we have $a(3) = nd_{\mathrm{L}} + 2d_{\mathrm{S}}$, $b = d_{\mathrm{L}}$ and

$p(3) = (nd_{\mathrm{L}} + 2d_{\mathrm{S}})/d_{\mathrm{L}}$. The effective average mobility for the bidisperse ferrofluid can be expressed as

$$\frac{\langle M\rangle}{\langle M_0\rangle} = \frac{1}{\sum\limits_{k=1}^{\infty}\left(g(1,k,0)+g(2,k,1)+g(3,k,2)\right)+g(4,0,1)} \cdot$$

$$\times\left\{\sum_{k=2}^{\infty}\left[g(1,k,0)\left(\frac{G_a(p(1))+G_b(p(1))}{2}\right)^{-1}\right]+g(1,1,0)+\right.$$

$$+\sum_{k=1}^{\infty}\left[g(2,k,1)\left(\frac{G_a(p(2))+G_b(p(2))}{2}\right)^{-1}+\right.$$

$$\left.\left.+g(3,k,2)\left(\frac{G_a(p(3))+G_b(p(3))}{2}\right)^{-1}\right]+g(4,0,1)\right\},$$

where $g(4,0,1)$ corresponds to single small particles.

We investigate the average mobility of the monodisperse system as a function of the magnetic dipole-dipole interaction parameter (Fig. 1*a*) and the particle concentration (Fig. 1*b*). In Fig. 1*a*, it is seen that the average mobility decreases with the increasing magnetic dipole-dipole interaction parameter. The parameter varies from $\lambda = 1$ to $\lambda = 5$. Three curves in the figure correspond to three different particle concentrations. The solid line is the average mobility of a system with the particle concentration $\rho = 0.05$. The dashed line corresponds to the particle concentration $\rho = 0.1$. The dashed-dotted line describes the effective mobility of a system with the particle concentration $\rho = 0.15$. We can say that with the increasing magnetic dipole-dipole interaction parameter the particles' chain formation increases. This leads to the growth of the average chain length, so that the effective average mobility decreases.

In Fig. 1*b*, the effective average mobility of the monodisperse system is presented as a function of the particle concentration. It is seen that the average mobility also decreases with the increasing particle concentration. In this case, the particle concentration is varied from $\rho = 0.001$ to $\rho = 0.15$. The curves correspond to different magnetic dipole-dipole interaction parameter values. The solid line illustrates the change of the effective average mobility independence on the particle concentration for the magnetic dipole-dipole interaction parameter $\lambda = 1$. The dotted line corresponds to the magnetic dipole-dipole interaction parameter $\lambda = 2$. The dashed line is the effective average mobility for the magnetic dipole-dipole interaction parameter $\lambda = 3$. The dashed-dotted line stands for $\lambda = 4$, and the line composed of rhombuses is the effective average mobility for the magnetic dipole-dipole interaction parameter $\lambda = 5$. Thus, with the increasing number of particles in the system, the average chain length increases for every value of λ, so the effective average mobility decreases similarly to the previous case.

For the bidisperse system, we investigated the effective averaged mobility as a function of the small particle concentration. The large particle concentration is related to $\rho_{\mathrm{L}} = 0.05$, while the small particle concentration varies from $\rho_{\mathrm{S}} = 0$ to $\rho_{\mathrm{S}} = 0.05$. We have chosen a typical model system consisting of small and large particles with the magnetic dipole-dipole interaction parameters $\lambda_{\mathrm{SS}} = 1$ for a small-small particle pair and $\lambda_{\mathrm{LL}} = 3$ for a large-large particle pair. So, we obtain the following system parameters, assuming that the non-magnetic layer on the surface of each particle is 2 nm thick: the small particle diameter (including the 2 nm layer) is $d_{\mathrm{S}} = 11.592$ nm, the large particle diameter (including the

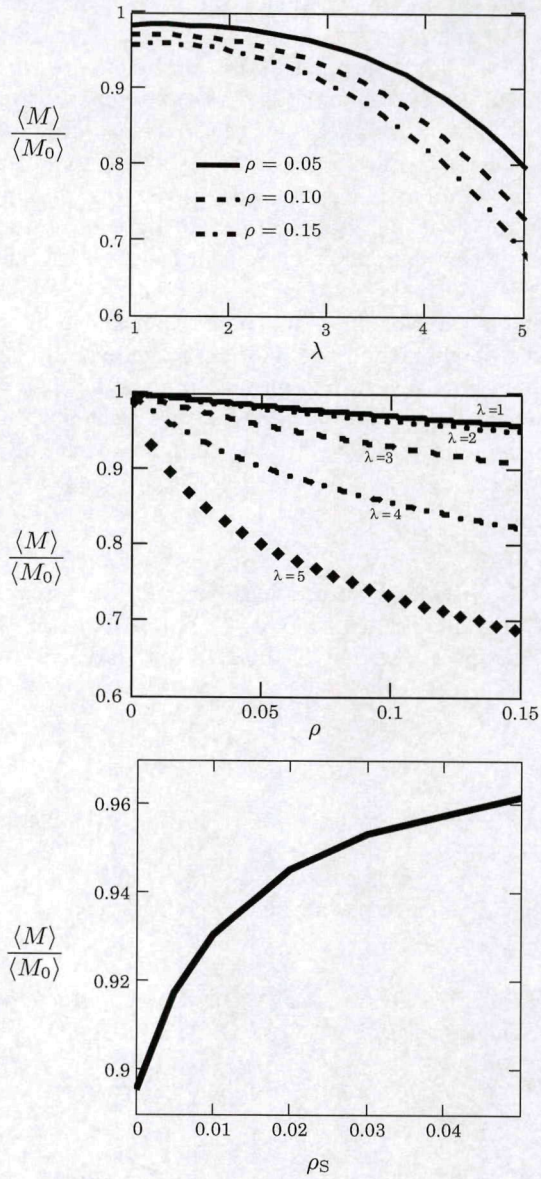

Fig. 1. Averaged mobility (*a*) for the monodisperse system as a function of the magnetic dipole-dipole interaction parameter; (*b*) for the monodisperse system as a function of the particle concentration; (*c*) for the bidisperse system as a function of the small particle concentration.

2 nm layer) is $d_{\mathrm{L}} = 15.614$ nm, the value of the magnetic dipole-dipole interaction parameter for the small-large particles pair is $\lambda_{\mathrm{SL}} = 1.698$. It is seen in Fig. 1*c* that the effective average mobility of the bidisperse system increases with the increase of the small particle concentration. Thus, when the total number of particles in the system grows, unlike the monodisperse case, the total effective mobility becomes higher. This is the consequence of the poisoning effect [17]. In other words, it is known that the average chain length might decrease with the increasing small particle density for the bidisperse model ferrofluid. This chain length decrease is the origin for the increasing particle mobility.

4. Conclusions. Many factors influence the system mobility, which is one of the key parameters in the gradient-induced diffusion. In this work, we have investigated the influence of polydispersity and cluster size distribution on the self-diffusion in magnetic fluids. In monodisperse systems, a strong decrease of the effective average mobility is found when the magnetic dipole-dipole interaction parameter and the particle concentration grow. In the monodisperse case, this is the consequence of the chain formation, whose intensity is strongly enhanced by the growing magnetic dipole-dipole interaction and by the ferroparticle density. Naturally, the growth of the average chain length leads to the effective average mobility decrease. In the bidisperse system, on the contrary, we observe an opposite tendency: the effective average mobility increases with the increasing density of small particles. This phemomenon occurs due to the overall chain shortening. Thus, it has been shown how the granulometric composition can change the behaviour of self-diffusion in magnetic fluids. We also expect a strong influence of the fractional composition on the gradient diffusion in magnetic colloids with chain aggregates. In our current research, we address this problem for both field and concentration gradients.

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